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THE SEPARATION AND GRAVIMETRIC ESTIMATION OF POTÁSSIUM.

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The market value of chloroplatinic acid, particularly under present conditions, is so high as to warrant a careful search for some cheaper reagent for the determination of potassium. Serullas[1], as early as 1831, proposed taking advantage of the insolubility of potassium perchlorate in concentrated alcoholic solutions and applying it as a reagent for the estimation of potassium. Unfortunately his proposal did not receive the attention it deserved because a convenient method for the preparation of perchloric acid had not at that time been worked out. Lately, Kreider[2] elaborated a method for the preparation of perchloric acid in large enough quantities and in sufficient purity to attempt its use as a precipitant for potassium. Following the treatment suggested by Caspari[3] he obtained very satisfactory results.[2]

The method was improved and simplified by Willard[4] in 1912, enabling one to obtain a very pure product in a comparatively short time. This revived old hopes and work was started by some of the Station chemists to study its merits as a substitute for chloroplatinic acid.

T. D. Jarrell[5] conducted some co-operative work in collaboration with other station chemists on some commercial products, the object being a comparison of results obtained by the official method and the perchlorate method. Ten investigators reported varying results on both methods, and the conclusion[6] reached was that the perchlorate method in its present form for determining potash in mixed fertilizers is very unsatisfactory, consuming too much time, and demanding removal of sulfuric acid with barium chloride in case the former is present, and that unless sufficient perchloric acid is added to combine with barium chloride to form perchlorate, the barium is not washed out from the potassium perchlorate precipitate with the alcohol wash, and further that potassium perchlorate is somewhat soluble[6] in the alcohol wash.

Baxter and Kobayashi[7] on the other hand, have shown that by careful manipulation and on use of absolute alcohol at low temperature satisfactory results can be obtained.

Hill[8] has shown that aniline perchlorate, which is easily prepared from aniline oil and perchloric acid, has a definite composition and contains no water of crystallization. A known amount of these crystals dissolved in a measured amount of absolute alcohol will, according to Hill, precipitate potassium quantitatively as perchlorate. His negative errors average 0.0004 grams K_2O. When, however, this is calculated into per cent error, it amounts to over 1.5 per cent. An explanation for the negative errors, according to Hill, is the incomplete conversion of KCl into $KClO_4$.

As the writer recently had occasion to run a large number of potassium determinations on the ash of forage plants and animal carcasses, the use of aniline perchlorate was tried under varying conditions. According to the writer's experience, the results are the best when the following points are observed.

The exact strength of the alcohol used must be known, and none used that runs below 99.5[8] per cent. For every 1.5 cc of water used for dissolving the mixed chlorides, 50 cc of absolute alcohol should be added. A weighed amount of aniline perchlorate dissolved in 50 cc of absolute alcohol must be added to the dissolved chlorides drop by drop with constant shaking and set aside for one hour before filtering. Under these conditions the writer succeeded in obtaining the following results.

PRECIPITATION OF POTASSIUM* WITH ANILINE PERCHLORATE.

No. of Expt.	Wt. of KCl taken Gms.	Corresponding Wt. taken of		Wt. of $KClO_4$ found gms.	Corresponding Wt. found of		Error in K_2O Gms.
		K_2O Gms.	$KClO_4$ Gms.		KCl Gms.	K_2O Gms.	
1	0.2005	0.1267	0.3726	0.3670	0.1975	0.1247	0.0020
2	0.2005	0.1267	0.3726	0.3685	0.1983	0.1252	0.0015
3	0.2000	0.1264	0.3716	0.3675	0.1978	0.1250	0.0014
4	0.2000	0.1264	0.3716	0.3670	0.1975	0.1247	0.0017
5	0.2000	0.1264	0.3716	0.3677	0.1972	0.1250	0.0014
6	0.2000	0.1264	0.3716	0.3676	0.1979	0.1249	0.0015
7	0.2000	0.1264	0.3716	0.3690	0.1986	0.1254	0.0010
8	0.2000	0.1264	0.3716	0.3680	0.1981	0.1251	0.0013
9	0.1000	0.0632	0.1858	0.1844	0.0993	0.0627	0.0005
10	0.1000	0.0632	0.1856	0.1840	0.0991	0.0626	0.0006
11	0.1000	0.0632	0.1856	0.1845	0.0994	0.0628	0.0004
12	0.1000	0.0632	0.1856	0.1843	0.0993	0.0627	0.0005

*The potassium chloride used was recrystallized from the commercial c. p. product. When it was estimated as chloroplatinate, it showed a purity of 99.9 per cent KCl.

The main objections to the perchlorate method at present are the time[8] required and the slight solubility of potassium perchlorate in 95 per cent alcohol. The use of aniline perchlorate in place of perchloric acid shortens the process to such an extent as to make it decidedly advantageous over all the processes in use for the separation and estimation of potassium. Moreover it affords the best means for direct quantitative separation and estimation of sodium in the alcoholic filtrate.

As to the solubility of $KClO_4$ in 95 per cent alcohol, the writer's experience, in applying this method to the estimation of sodium and potassum in the ash of forage plants and animal carcasses, has been that some potassium chloride is occluded in the perchlorate. This is shown by the fact that higher results are obtained if the precipitate is allowed to stand for about two hours before filtration. Three series of four experiments each were conducted to establish this point. When the precipitant, dissolved in the proper amount of alcohol, was added all at once and filtered within fifteen minutes, decidedly lower results were obtained, but when the precipitant was added drop by drop with constant shaking and allowed to stand about two hours before filtration, the results were decidedly better. If it were simply a matter of solubility, no better results could be expected under the latter conditions. The potassium chloride which seems to adhere persistently to the perchlorate, being soluble in alcohol, is of course washed off gradually with the alcohol wash. Jarrell, in summing up his experience with regard to the solubility of potassium perchlorate, does not state whether he obtained the theoretical yield when he prepared the potassium perchlorate from potassium chloride.

The writer is inclined to believe that under the conditions Jarrell's precipitates were contaminated with potassium chloride. A careful observation of the table shown in this paper will illustrate the fact more clearly. In experiments 9, 10, 11 and 12, 0.1 gram of KCl was used instead of 0.2 gram. Exactly the same amount of water and alcohol were used and the same procedure followed, but the negative errors in this case are low enough to be within experimental error. These results clearly tend to show that when sufficient precautions are taken to prevent occlusion during the conversion of the chlorides into perchlorate, a complete precipitation may be expected.

Taking into consideration the fact sufficient chloroplatinic acid must be added to combine with all the bases present in order to be washable by the alcohol wash, the necessity of finding a cheaper substitute is at once appreciated. In the writer's opinion, aniline perchlorate is the best reagent to replace the highly expensive platinic chloride for the separation and estimation of potassium. It is easily prepared, is much cheaper and is easy to handle.

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